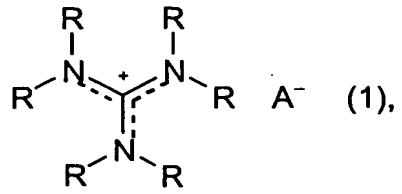
Patent Claims

1. Process for the preparation of guanidinium salts of the formula (1)



(1),

in which the substituents R in each case, independently of one another, have the meaning of

hydrogen,

straight-chain or branched alkyl having 1-20 C atoms,

saturated, partially or fully unsaturated cycloalkyl having 3-7 C atoms, which may be substituted by alkyl groups having 1-6 C atoms,

where one or more substituents R may be partially or fully substituted by halogen or partially by CN or NO_2 and halogen denotes F, Cl, Br or I,

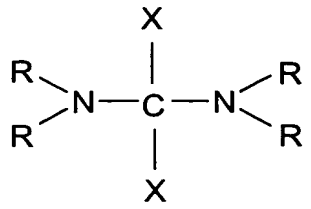
where up to four substituents R may be bonded to one another in pairs by a single or double bond

and where a carbon atom or two non-adjacent carbon atoms of one or more substituents R may be replaced by atoms and/or atom groups selected from the group -O-, -C(O)-, -C(O)O-, -S-, -S(O)-, $-SO_2-$, $-SO_3-$, -N=, -N=N-, -NH-, -NR'-, -PR'-, -P(O)R'-, -P(O)R'-O-, -O-P(O)R'-O-, and $-P(R')_2=N-$, where R' denotes non-fluorinated, partially or perfluorinated alkyl having 1-6 C atoms, saturated or partially unsaturated cycloalkyl having 3-7 C atoms, unsubstituted or substituted phenyl or an unsubstituted or substituted heterocycle

and

A^- is a sulfonate, alkyl- or arylsulfate, hydrogensulfate, imide, methanide, carboxylate, phosphate, phosphinate, phosphonate, borate, thiocyanate, perchlorate, fluorosilicate or nitrate,

by reaction of a compound of the formula (2)



(2)

,

in which the substituents R have a meaning indicated for formula (1) and X denotes F, Cl or Br,

with a compound of the formula (3)

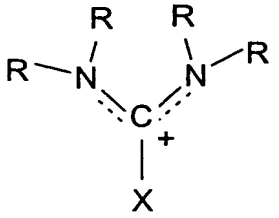
$Kt^+ A^-$ (3),

in which A^- has a meaning indicated for formula (1) and

Kt^+ can be a proton, R''_3Si, an alkali or alkaline earth metal cation, an ammonium cation, a phosphonium cation or a cation from group 11 or 12,

where R'' in each case, independently of one another, denotes phenyl or a linear or branched alkyl group having 1-6 C atoms, which may be substituted by phenyl,

and subsequent reaction of the resultant compound of the formula (4)

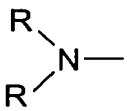


A^- (4)

,

where the substituents R, X and A^- have a meaning indicated for formula (1) or (2),

with compounds of the formula (5)



(5)

,

where the substituents R have a meaning indicated for formula (1) and M denotes hydrogen, R''_3Si, an alkali or alkaline earth metal and

R'' in each case, independently of one another, denotes phenyl or a linear or branched alkyl group having 1-6 C atoms, which may be substituted by phenyl.

2. Process according to Claim 1, characterised in that compounds of the formula $Kt^+ A^-$ (3) are employed, in which Kt^+ has a meaning indicated in Claim 1 and

A^- is selected from the group

$[R^1OSO_3]^-$, $[R^1SO_3]^-$, $[R^FSO_3]^-$, $[(FSO_2)_2N]^-$, $[(R^FSO_2)_2N]^-$, $[(R^FSO_2)(R^FCO)N]^-$, $[(R^FSO_2)_3C]^-$, $[(FSO_2)_3C]^-$, $[R^1CH_2C(O)O]^-$, $[R^FC(O)O]^-$, $[P(C_nF_{2n+1-m}H_m)_yF_{6-y}]^-$, $[P(C_6F_5)_yF_{6-y}]^-$, $[(R^1O)_2P(O)O]^-$, $[R^1{}_2P(O)O]^-$, $[R^1P(O)O_2]^{2-}$, $[R^F{}_2P(O)O]^-$, $[R^FP(O)O_2]^{2-}$, $[BF_{4-z}R^F{}_z]^-$, $[BF_{4-z}(CN)_z]^-$, $[B(C_6F_5)_4]^-$, $[B(OR^1)_4]^-$, $[N(CN)_2]^-$, $[C(CN)_3]^-$, $[N(CF_3)_2]^-$, $[HSO_4]^-$, $[SiF_6]^{2-}$, $[ClO_4]^-$, $[SCN]^-$ and $[NO_3]^-$,

in which the substituents R^F in each case, independently of one another, have the meaning of

perfluorinated and straight-chain or branched alkyl having 1-20 C atoms, perfluorinated and straight-chain or branched alkenyl having 2-20 C atoms and one or more double bonds,

perfluorinated and saturated, partially or fully unsaturated cycloalkyl having 3-7 C atoms, which may be substituted by perfluoroalkyl groups, where the substituents R^F may be bonded to one another in pairs by a single or double bond and

where a carbon atom or two non-adjacent carbon atoms of the substituent R^F which are not in the α-position to the heteroatom may be replaced by atoms and/or atom groups selected from the group -O-, -C(O)-, -S-, -S(O)-, $-SO_2-$, -N=, -N=N-, -NR'-, -PR'- and -P(O)R'-, where R' denotes non-fluorinated, partially or perfluorinated alkyl having 1-6 C atoms, saturated or partially unsaturated cycloalkyl having 3-7 C atoms, unsubstituted or substituted phenyl or an unsubstituted or substituted heterocycle,

in which the substituents R^1 in each case, independently of one another, have the meaning of

straight-chain or branched alkyl having 1-20 C atoms,

straight-chain or branched alkenyl having 2-20 C atoms and one or more double bonds,

straight-chain or branched alkynyl having 2-20 C atoms and one or more triple bonds,

saturated, partially or fully unsaturated cycloalkyl having 3-7 C atoms, which may be substituted by alkyl groups having 1-6 C atoms,

where the substituents R^1 may be partially substituted by CN, NO_2 or halogen and

halogen denotes F, Cl, Br or I,

where the substituents R^1 may be bonded to one another in pairs by a single or double bond and

where a carbon atom or two non-adjacent carbon atoms of the substituent R^1 which are not in the α-position to the heteroatom may be replaced by atoms and/or atom groups selected from the group -O-, -C(O)-, -C(O)O-, -S-, -S(O)-, $-SO_2-$, $-SO_3-$, -N=, -N=N-, -NH-, -NR'-, -PR'-, -P(O)R'-, P(O)R'O-, OP(O)R'O-, $-PR'_2=N-$, -C(O)NH-, -C(O)NR'-, $-SO_2NH-$ or $-SO_2NR'-$, where R' denotes non-fluorinated, partially or perfluorinated alkyl having 1-6 C atoms, saturated or partially unsaturated cycloalkyl having 3-7 C atoms, unsubstituted or substituted phenyl or an unsubstituted or substituted heterocycle

and the variables

n denotes 1 to 20,

m denotes 0, 1, 2 or 3,

y denotes 0, 1, 2, 3 or 4, and

z denotes 0, 1, 2, 3 or 4.

3. Process according to Claim 1 or 2, characterised in that A^- is selected from the group
$[CH_3OSO_3]^-$, $[C_2H_5OSO_3]^-$, $[C(CN)_3]^-$,
$[CH_3SO_3]^-$, $[C_8H_{17}SO_3]^-$, $[CH_3C_6H_4SO_3]^-$, $[CF_3SO_3]^-$, $[C_2H_5SO_3]^-$,
$[CF_3CF_2SO_3]^-$, $[(CF_3SO_2)_2N]^-$, $[(FSO_2)_2N]^-$, $[(CF_3SO_2)(CF_3CO)N]^-$,
$[(C_2F_5SO_2)(CF_3CO)N]^-$, $[(C_2F_5SO_2)_2N]^-$, $[(CF_3SO_2)_3C]^-$, $[(C_2F_5SO_2)_3C]^-$,
$[(FSO_2)_3C]^-$, $[CH_3C(O)O]^-$, $[C_2H_5C(O)O]^-$, $[CF_3C(O)O]^-$,
$[CF_3CF_2C(O)O]^-$, $[PF_6]^-$, $[P(C_2F_5)_3F_3]^-$, $[P(C_4F_9)_3F_3]^-$, $[P(CF_3)_3F_3]^-$,
$[P(C_2F_4H)(CF_3)_2F_3]^-$, $[P(C_2F_3H_2)_3F_3]^-$, $[P(C_2F_5)(CF_3)_2F_3]^-$, $[P(C_6F_5)_3F_3]^-$,
$[P(C_3F_7)_3F_3]^-$, $[P(C_2F_5)_2F_4]^-$, $[(HO)_2P(O)O]^-$, $[(CH_3O)_2P(O)O]^-$,
$[(C_2H_5O)_2P(O)O]^-$, $[(C_2F_5)_2P(O)O]^-$, $[(C_2F_5)P(O)O_2]^{2-}$, $[P(C_6F_5)_2F_4]^-$,
$[(CH_3)_2P(O)O]^-$, $[CH_3P(O)O_2]^{2-}$, $[(CF_3)_2P(O)O]^-$, $[CF_3P(O)O_2]^{2-}$, $[BF_4]^-$,
$[BF_3(CF_3)]^-$, $[BF_2(C_2F_5)_2]^-$, $[BF_3(C_2F_5)]^-$, $[BF_2(CF_3)_2]^-$, $[B(C_2F_5)_4]^-$,
$[BF_3(CN)]^-$, $[BF_2(CN)_2]^-$, $[B(CN)_4]^-$, $[B(OCH_3)_4]^-$, $[B(CF_3)_4]^-$,
$[B(OCH_3)_2(OC_2H_5)_2]^-$, $[B(O_2C_2H_4)_2]^-$, $[B(O_2C_2H_2)_2]^-$, $[B(O_2C_6H_4)_2]^-$,
$[N(CN)_2]^-$, $[N(CF_3)_2]^-$, $[HSO_4]^-$, $[ClO_4]^-$, $[SiF_6]^-$, $[SCN]^-$ or $[NO_3]^-$.

4. Process according to one or more of Claims 1 to 3, characterised in that the substituent X in dihalogen compounds of the formula (2) according to Claim 1 denotes fluorine or chlorine.

5. Process according to one or more of Claims 1 to 4, characterised in that the substituent R in compounds of the formula (5) according to Claim 1 in each case, independently of one another, has the meaning of
hydrogen,
straight-chain or branched alkyl having 1-20 C atoms or
saturated, partially or fully unsaturated cycloalkyl having 3-7 C atoms, which may be substituted by alkyl groups having 1-6 C atoms.

6. Process according to one or more of Claims 1 to 5, characterised in that the first step of the process is carried out in water.

7. Process according to one or more of Claims 1 to 6, characterised in that the first step of the process is carried out at temperatures of 0° to 150°C.

8. Process according to one or more of Claims 1 to 5, characterised in that the first step of the process is carried out in an organic solvent.

9. Process according to one or more of Claims 1 to 5 and 8, characterised in that the first step of the process is carried out at temperatures of -50° to 150°C.

10. Process according to one or more of Claims 1 to 9, characterised in that the second step of the process is carried out without a solvent.

11. Process according to one or more of Claims 1 to 10, characterised in that the second step of the process is carried out at a temperature at which at least one component is liquid.

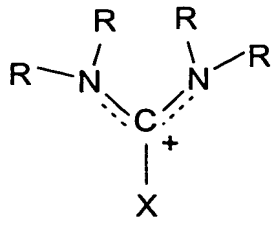
12. Process according to one or more of Claims 1 to 9, characterised in that the second step of the process is carried out in an organic solvent.

13. Process according to one or more of Claims 1 to 9 and 12, characterised in that the second step of the process is carried out at temperatures of -50° to 150°C.

14. Process according to one or more of Claims 1 to 9, characterised in that the second step of the process is carried out in water.

15. Process according to one or more of Claims 1 to 9 and 14, characterised in that the second step of the process is carried out at temperatures of 0° to 150°C.

16. Compounds of the formula (4)



A^- (4)

,

in which the substituents R in each case, independently of one another, have the meaning of

hydrogen,

straight-chain or branched alkyl having 1-20 C atoms,

saturated, partially or fully unsaturated cycloalkyl having 3-7 C atoms, which may be substituted by alkyl groups having 1-6 C atoms,

where one or more substituents R may be partially or fully substituted by halogen or partially by CN or NO_2 and

halogen denotes F, Cl, Br or I,

where up to four substituents R may be bonded to one another in pairs by a single or double bond

and where a carbon atom or two non-adjacent carbon atoms of one or more substituents R may be replaced by atoms and/or atom groups selected from the group -O-, -C(O)-, -C(O)O-, -S-, -S(O)-, $-SO_2-$, $-SO_3-$, -N=, -N=N-, -NH-, -NR'-, -PR'-, -P(O)R'-, -P(O)R'-O-, -O-P(O)R'-O-, and $-P(R')_2=N-$, where R' denotes non-fluorinated, partially or perfluorinated alkyl having 1-6 C atoms, saturated or partially unsaturated cycloalkyl having 3-7 C atoms, unsubstituted or substituted phenyl or an unsubstituted or substituted heterocycle,

X denotes F, Cl or Br,

with the proviso that all four substituents R are not simultaneously hydrogen and

A^- is selected from the group

$[R^1OSO_3]^-$, $[R^1SO_3]^-$, $[R^FSO_3]^-$, $[(FSO_2)_2N]^-$, $[(R^FSO_2)_2N]^-$, $[(R^FSO_2)(R^FCO)N]^-$, $[(R^FSO_2)_3C]^-$, $[(FSO_2)_3C]^-$, $[R^1CH_2C(O)O]^-$, $[R^FC(O)O]^-$, $[P(C_nF_{2n+1-m}H_m)_yF_{6-y}]^-$, $[P(C_6F_5)_yF_{6-y}]^-$, $[(R^1O)_2P(O)O]^-$, $[R^1{}_2P(O)O]^-$, $[R^1P(O)O_2]^{2-}$, $[R^F{}_2P(O)O]^-$, $[R^FP(O)O_2]^{2-}$, $[BF_{4-z}R^F{}_z]^-$,

$[BF_{4-z}(CN)_z]^-$, $[B(C_6F_5)_4]^-$, $[B(OR^1)_4]^-$, $[N(CN)_2]^-$, $[(CN_3)C]^-$, $[N(CF_3)_2]^-$, $[HSO_4]^-$, $[SiF_6]^{2-}$, $[ClO_4]^-$, $[SCN]^-$ and $[NO_3]^-$,

where $[CF_3SO_3]^-$ is excepted and

in which the substituents R^F in each case, independently of one another, have the meaning of

perfluorinated and straight-chain or branched alkyl having 1-20 C atoms,

perfluorinated and straight-chain or branched alkenyl having 2-20 C atoms and one or more double bonds,

perfluorinated and saturated, partially or fully unsaturated cycloalkyl having 3-7 C atoms, which may be substituted by perfluoroalkyl groups,

where the substituents R^F may be bonded to one another in pairs by a single or double bond and

where a carbon atom or two non-adjacent carbon atoms of the substituent R^F which are not in the α-position to the heteroatom may be replaced by atoms and/or atom groups selected from the group -O-, -C(O)-, -S-, -S(O)-, $-SO_2-$, -N=, -N=N-, -NR'-, -PR'- and -P(O)R'-, where R' denotes non-fluorinated, partially or perfluorinated alkyl having 1-6 C atoms, saturated or partially unsaturated cycloalkyl having 3-7 C atoms, unsubstituted or substituted phenyl or an unsubstituted or substituted heterocycle,

in which the substituents R^1 in each case, independently of one another, have the meaning of

straight-chain or branched alkyl having 1-20 C atoms,

straight-chain or branched alkenyl having 2-20 C atoms and one or more double bonds,

straight-chain or branched alkynyl having 2-20 C atoms and one or more triple bonds,

saturated, partially or fully unsaturated cycloalkyl having 3-7 C atoms, which may be substituted by alkyl groups having 1-6 C atoms,

where the substituents R^1 may be partially substituted by CN, NO_2 or halogen and
halogen denotes F, Cl, Br or I,
where the substituents R^1 may be bonded to one another in pairs by a single or double bond and
where a carbon atom or two non-adjacent carbon atoms of the substituent R^1 which are not in the α-position to the heteroatom may be replaced by atoms and/or atom groups selected from the group -O-, -C(O)-, -C(O)O-, -S-, -S(O)-, $-SO_2-$, $-SO_3-$, -N=, -N=N-, -NH-, -NR'-, -PR'-, -P(O)R'-, P(O)R'O-, OP(O)R'O-, $-PR'_2=N-$, -C(O)NH-, -C(O)NR'-, $-SO_2NH-$ or $-SO_2NR'-$, where R' denotes non-fluorinated, partially or perfluorinated alkyl having 1-6 C atoms, saturated or partially unsaturated cycloalkyl having 3-7 C atoms, unsubstituted or substituted phenyl or an unsubstituted or substituted heterocycle
and the variables

n denotes 1 to 20,
m denotes 0, 1, 2 or 3,
y denotes 1, 2, 3 or 4 and
z denotes 1, 2, 3 or 4.

17. Compounds according to Claim 16, characterised in that the substituents R denote hydrogen or a straight-chain or branched alkyl group having 1-12 C atoms,
with the proviso that all four substituents R are not hydrogen or at least two substituents R are bonded to one another by single or double bonds in such a way that a monocyclic cation is formed and
the counteranion A^- denotes
$[CH_3OSO_3]^-$, $[C_2H_5OSO_3]^-$, $[C(CN)_3]^-$,
$[CH_3SO_3]^-$, $[C_8H_{17}SO_3]^-$, $[CH_3C_6H_4SO_3]^-$, $[CF_3SO_3]^-$, $[C_2H_5SO_3]^-$,
$[CF_3CF_2SO_3]^-$, $[(CF_3SO_2)_2N]^-$, $[(FSO_2)_2N]^-$, $[(CF_3SO_2)(CF_3CO)N]^-$,
$[(C_2F_5SO_2)(CF_3CO)N]^-$, $[(C_2F_5SO_2)_2N]^-$, $[(CF_3SO_2)_3C]^-$, $[(C_2F_5SO_2)_3C]^-$,

$[(FSO_2)_3C]^-$, $[CH_3C(O)O]^-$, $[C_2H_5C(O)O]^-$, $[CF_3C(O)O]^-$, $[CF_3CF_2C(O)O]^-$, $[PF_6]^-$, $[P(C_2F_5)_3F_3]^-$, $[P(C_4F_9)_3F_3]^-$, $[P(CF_3)_3F_3]^-$, $[P(C_2F_4H)(CF_3)_2F_3]^-$, $[P(C_2F_3H_2)_3F_3]^-$, $[P(C_2F_5)(CF_3)_2F_3]^-$, $[P(C_6F_5)_3F_3]^-$, $[P(C_3F_7)_3F_3]^-$, $[P(C_2F_5)_2F_4]^-$, $[(HO)_2P(O)O]^-$, $[(CH_3O)_2P(O)O]^-$, $[(C_2H_5O)_2P(O)O]^-$, $[(C_2F_5)_2P(O)O]^-$, $[(C_2F_5)P(O)O_2]^{2-}$, $[P(C_6F_5)_2F_4]^-$, $[(CH_3)_2P(O)O]^-$, $[CH_3P(O)O_2]^{2-}$, $[(CF_3)_2P(O)O]^-$, $[CF_3P(O)O_2]^{2-}$, $[BF_4]^-$, $[BF_3(CF_3)]^-$, $[BF_2(C_2F_5)_2]^-$, $[BF_3(C_2F_5)]^-$, $[BF_2(CF_3)_2]^-$, $[B(C_2F_5)_4]^-$, $[BF_3(CN)]^-$, $[BF_2(CN)_2]^-$, $[B(CN)_4]^-$, $[B(OCH_3)_4]^-$, $[B(CF_3)_4]^-$, $[B(OCH_3)_2(OC_2H_5)_2]^-$, $[B(O_2C_2H_4)_2]^-$, $[B(O_2C_2H_2)_2]^-$, $[B(O_2C_6H_4)_2]^-$, $[N(CN)_2]^-$, $[N(CF_3)_2]^-$, $[HSO_4]^-$, $[ClO_4]^-$, $[SiF_6]^-$, $[SCN]^-$ or $[NO_3]^-$.